

CLAIMS

1. Method for continuously coating a substrate in motion such as a metal strip made of steel, the coating formed being an ultra-fine film of a thickness of
5 between 10 and 100nm, deposited on the substrate:
- from a solution containing nanoparticles of oxides,
 - in conditions of controlled pH,
 - said substrate being at a temperature higher than 120°C,
 - the total duration of the deposition being less than 5
10 seconds, preferably less than 1 second,
- characterised in that at least one chemical additive, called a "refiner", is incorporated into said solution, said refiner having, mutatis mutandis, the effect of restricting the formation of said coating.
- 15 2. Method according to Claim 1, characterised in that that substrate to be coated is either a bare metal, preferably steel, stainless steel (or "inox"), aluminium, zinc or copper, or a first metal coated with a second metal, preferably a strip of steel coated with a layer
20 of zinc, aluminium, tin or an alloy of at least two of these metals.
3. Method according to Claim 1 or 2, characterised in that the nanoparticles comprise oxides, preferably SiO₂, TiO₂, ZrO₂, Al₂O₃, CeO₂, Sb₂O₅, Y₂O₃, ZnO, SnO₂
25 or mixtures of these oxides, are hydrophilic and/or hydrophobic, have a size of between 1 and 100nm and are in the solution with a content of between 0.1 and 10%, and preferably between 0.1 and 1%.
4. Method according to any of Claims 1 to
30 3, characterised in that the concentration of refiner is between 1 and 20 g per litre (g/L) of solution, preferably between 5 and 10g/L.
5. Method according to Claim 4, characterised in that the refiner used for the deposition of
35 nanoparticles of silica is selected from the group of

compounds comprising catechin and its derivatives, hydrofluoric and boric acids, borates, sodium and potassium carbonates and hydrogen carbonates, ammonium hydroxide and amines that are soluble in water.

5 6. Method according to Claim 4, characterised in that the refiner used for a deposition of nanoparticles of stannous or stannic oxide is selected from the group of compounds comprising borates, potassium carbonates and hydrogen carbonates, ammonium hydroxide and
10 amines that are soluble in water.

 7. Method according to Claim 4, characterised in that the refiner used for a deposition of nanoparticles of cerium and zirconium oxides is selected from the group comprising hydrofluoric, boric and carboxylic
15 acids.

 8. Method according to Claim 7, characterised in that the refiner used for a deposition of nanoparticles of cerium and zirconium oxides is selected from the group of compounds comprising formic, ascorbic, ascorbic
20 and citric acids.

 9. Method according to any one of the proceeding claims, characterised in that the pH of the solution is adjusted so as to allow the pickling of surface oxides from the metal substrate when it is in contact with
25 the solution, to give a maximum electrical charge to the particles in order to avoid any agglomeration in the solution and to make the particles as reactive as possible without destabilising the solution.

 10. Method according to Claim 9,
30 characterised in that the pH of the solutions based on nanoparticles of SiO_2 , SnO_2 , TiO_2 , ZnO or Sb_2O_5 is alkaline and is preferably between 9 and 13.

 11. Method according to Claim 9, characterised in that the pH of the solutions based on

nanoparticles of ZrO_2 , CeO_2 , SiO_2 or Sb_2O_5 is acidic and is preferably between 1 and 5.

12. Method according to Claim 10 or 11, characterised in that the pH of the solutions based on a mixture of nanoparticles is adjusted so that the solution is stable through time.

13. Method according to Claim 9, characterised in that, in the case of a surface layer of the substrate containing a component of zinc, aluminium, iron, tin, chrome, nickel or copper, the pH is alkaline.

14. Method according to Claim 9, characterised in that, in the case of a surface layer of the substrate containing a component of zinc, aluminium, iron, tin, chrome, nickel or copper, the pH of the solution is acidic.

15. Method according to Claim 1, characterised in that the deposit is formed by immersion of the substrate for a controlled period of time in an immersion tank comprising the solution.

16. Method according to Claim 1, characterised in that the deposit is formed by spraying the solution onto the substrate by means of a nozzle, i.e. a device, assisted or not, with gas under pressure, that sprays droplets of the solution.

17. Method according to Claim 1, characterised in that the deposit is formed by deposition of the solution on the substrate by means of a roller.

18. Method according to Claim 1, characterised in that the solution that comes into contact with the strip is kept at a temperature lower than 100°C and preferably lower than 80°C .

19. Method according to Claim 1, characterised in that the temperature of the substrate at the start of the deposition is higher than 125°C and lower than 250°C .

20. Method according to Claim 19, characterised in that, if the substrate already has a metallic coating before the treatment, the temperature of the substrate at the start of the deposition is higher than 125°C and lower by 30 to 100°C than the melting point of the coating metal.

21. Method according to Claim 20, characterised in that, if the substrate has a metallic coating made by immersion, as for example in galvanisation by immersion, the deposit is formed just after the deposition of the metallic coating, before the substrate cools down.

22. Method according to Claim 21, characterised in that, in the case of a substrate liable to a too-high level of oxidation for this to be eliminated during the deposition, the substrate is protected from excessive contact with air by means of a neutral gas such as nitrogen or argon.

23. Method according to Claim 20 or 21, characterised in that the deposition is limited in time by varying the depth of immersion in the case of deposition in a solution or the length sprayed in the case of spraying the solution with nozzles.

24. Method according to Claim 1, characterised in that the solution is an aqueous solution or comprises any other solvent capable of effectively dispersing said nanoparticles.

25. Method according to Claim 1, characterised in that agents for the improvement of resistance to corrosion and/or adhesion to the substrate or the paint and/or to improve the glide during formation are added to the solution.

26. Method according to Claim 1, characterised in that the coated substrate may be rinsed after post-treatment by means of water or of a solution based

on organic silanes or carboxylic acid with an ability to form a strong link with the organic.

27. Method according to Claim 1, characterised in that it comprises the means for:

- 5 - continuously measuring and regulating the pH,
- ensuring the replenishment of the solution and the elimination of surplus products of the reaction,
- ensuring the homogeneous mixture of the bath so as to avoid turbulence on its surface.

10 28. Method according to Claim 15, characterised in that temperatures of the strip and of the bath, the time the strip remains in the bath, the concentration of nanoparticles in the bath and the pH of the bath are controlled.

15 29. Method according to Claim 16, characterised in that the temperature of the strip, the length of spraying time, the concentration of nanoparticles in the solution sprayed, the spraying flow and the pH are controlled.

20 30. Installation for the coating of a steel strip, comprising a device for obtaining a second coating layer on a first coating layer formed by hot dipping or by spraying with jets, by implementation of the method according to any of the preceding claims, characterised in that said
25 installation is located after elements ensuring the spinning and solidification operations of the first coating layer, said second coating layer being formed in this installation at a temperature lower by at least 100°C than the temperature at which the first coating layer solidifies.

30 31. Flat or long metallurgical product, preferably a strip, wire, profiled section or tube, coated with an ultra-fine protective layer by means of the method according to any one of Claims 1 to 29, characterised in that said protective layer comprises nanoparticles of oxides or a
35 mixture of these oxides, preferably Al_2O_3 , Y_2O_3 , SiO_2 , SnO_2 ,

TiO₂, ZnO, Sb₂O₅, ZrO₂ or CeO₂, and has a thickness of less than 100nm.

32. Metallurgical product of the coated-strip type according to Claim 31, the thickness of which,
5 possibly the initial thickness before the profiled section or tube is produced, is between 0.15 and 5mm.